



DET NORSKE VERITAS

Final Report
Corrosion Integrity Threats in the
Transportation of Biodiesel

Pipeline & Hazardous Materials Safety Administration
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Corrosion Integrity Threats in the Transportation of Biodiesel	DET NORSKE VERITAS (U.S.A.), INC. Materials & Corrosion Technology Center 5777 Frantz Road Dublin, OH 43017-1386, United States Tel: (614) 761-1214 Fax: (614) 761-1633 http://www.dnv.com http://www.dnvcolumbus.com
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Executive Summary

Biodiesel (B100) is briefly defined as the monoalkyl esters of oils or fats. The demand for biodiesel and biodiesel blends as a fuel source has increased exponentially in the last decade. Today in the United States, nearly every Original Equipment Manufacturer (OEM) has approved the use of biodiesel blends of up to 5% (B5). According to the National Biodiesel Board (NBB), the yearly production of B100 has increased from approximately 0.5 million gallons in 1999 to 450 million in 2007. A current estimate indicates that nearly 170 biodiesel plants are operational in the U.S. as of 2008 with a projected production volume of 1.5 billion gallons (bg) by the end of 2009. In addition, new regulations will force a significant growth in biodiesel production during the next 5 years. The most recent Renewable Fuel Standards issued by the U.S. Environmental Protection Agency specifies a number of alternative biofuels, including corn-based ethanol, cellulosic ethanols, biodiesels, and other advanced biofuels that may be manufactured in the future using hitherto unknown technologies. The standard does not provide specific targets for biodiesel because the technology for its manufacture is still evolving. Significant research efforts are underway to manufacture biodiesel from algae. If successful, the biodiesel volumes could increase enormously, eclipsing other biofuels.

Pipeline transportation can save up to 20 cents a gallon of fuel transported over trucks and can result in other benefits such as lower greenhouse gas emissions and decreased hazards due to highway accidents. The benefits of pipeline transportation are predicated upon addressing all the integrity and operational issues.

Integrity threats for transportation of biodiesel and biodiesel fuel blends through pipelines have not been addressed explicitly. The corrosion resistance of common materials systems that the fuel would see regular incidence with has not been verified. The overarching goal of this work was to address these uncertainties as comprehensively as possible within a manageable scope of work. The work was divided up into three main technical tasks as listed below:

Task 2 – Corrosion Inhibition Performance

Task 3 – Integrity of Non-Ferrous Metallic System Components (Cu-alloys)

Task 4 – Integrity of Non-Metallic System Components (Elastomers)

Because PHMSA decided to terminate the project much earlier than the originally planned ending date, the work scope was adjusted to achieve the most valuable results obtainable in the truncated amount of time.



The key results based on the adjusted work scope are:

1. Literature survey on pipeline materials systems and precedence for degradation related work on those systems in biofuels.
2. Investigation of the plausibility of electrochemical measurement in biodiesel fuels.
3. Biodiesel corrosivity determined on pipe steel with and without the aid of commonly used petrodiesel inhibitors.



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1.0 BACKGROUND

Biodiesel (B100) is briefly defined as the monoalkyl esters of oils or fats [1]. The demand for biodiesel and biodiesel blends as a fuel source has increased exponentially in the last decade. Today in the United States, nearly every Original Equipment Manufacturer (OEM) has approved the use of biodiesel blends of up to 5% (B5) [2]. According to the National Biodiesel Board (NBB), the yearly production of B100 has increased from approximately 0.5 million gallons in 1999 to 450 million in 2007 [3]. A current estimate indicates that nearly 170 biodiesel plants are operational in the U.S. as of 2008 with a projected production volume of 1.5 billion gallons (bg) by the end of 2009 [4]. In addition, new regulations will force a significant growth in biodiesel production during the next 5 years. The most recent Renewable Fuel Standards issued by the U.S. Environmental Protection Agency [5] specifies a number of alternative biofuels, including corn-based ethanol, cellulosic ethanol, biodiesels, and other advanced biofuels that may be manufactured in the future using hitherto unknown technologies (Figure 1). The standard does not provide specific targets for biodiesel because the technology for its manufacture is still evolving. Significant research efforts are underway to manufacture biodiesel from algae. If successful, the biodiesel volumes could increase enormously, eclipsing other biofuels.

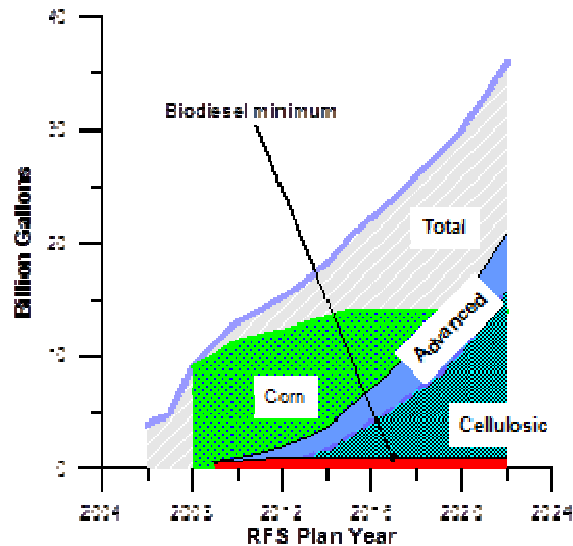


Figure 1. The U.S. Renewable Fuel Standard issued by EPA [5].

Pipeline transportation can save up to 20 cents a gallon of fuel transported over trucks and can result in other benefits such as lower greenhouse gas emissions and decreased hazards due to highway accidents. The benefits of pipeline transportation are predicated upon addressing all the integrity and operational issues.

Yet, integrity threats for transportation of biodiesel and biodiesel fuel blends through pipelines have not been addressed explicitly. The corrosion resistance of common materials systems that the fuel would see regular incidence with has not been verified.

B100 chemistry specification is contained in ASTM D6751-09 and it has been approved as a component in conventional diesel fuels at 5, 6, and 20 volume percent (B5, B6, and B20). A number of new biodiesel sources are anticipated in the future, such as from algae processing. These biodiesels will also have to meet ASTM D 6751, but may contain other constituents not listed in ASTM specifications. The only corrosion-related requirement in ASTM D6751 is the copper strip test (ASTM D130). The copper strip corrosivity test (ASTM D130) is a particularly poor test because it is qualitative, subjective, and it has no relevance to materials and conditions in pipelines. Therefore, corrosivity testing more relative pipeline materials systems with specific respect to biodiesel transportation is desirable. It is the aim of this research to address these issues as holistically as possible.

2.0 PROJECT OBJECTIVE

The overarching objective of this work is to address the uncertainties in materials degradation in biodiesel fuels with respect to specific pipeline integrity threats as comprehensively as possible within a manageable scope of work. The original scope was divided up into three main technical tasks summarized below:

Task 2 – Corrosion Inhibition Performance

Task 3 – Integrity of Non-Ferrous Metallic System Components (Cu-alloys)

Task 4 – Integrity of Non-Metallic System Components (Elastomers)

A kickoff meeting was held on June 16, 2010 with various stakeholders to discuss the project objectives and proposed tasks. Attendees included representatives from the National Biodiesel Board, representatives from several pipeline companies, PHMSA staff and a representative from the Steel Tank Institute (STI). The project team presented the objectives of the project, the different tasks, discussed the need to plan a matrix of tests and emphasized the need to obtain biodiesel and petrodiesel samples for the testing.

The matrix of tests was slightly augmented in September in a meeting with National Biodiesel Board representatives held at DNV. The emphasis on feedstock was introduced as a matrix dimension. Since PHMSA decided to terminate the project much earlier than the originally planned ending date, the work scope and the objective were modified based available time and maximization of previously expended efforts. The following tasks were accomplished:



Task 1: Literature survey of pipeline materials systems and precedence of interaction with biodiesel fuels; Viability of electrochemical measurement in biodiesel

Task 2: Corrosion inhibition performance evaluation in B100 and B0

Task 5: Final Report

Originally scoped tasks that were not addressed fully enough to report are:

Task 3: This task was intended to be a study of Cu-based alloys, such as brass, and their effect on the degradation of the fuel.

Task 4: This task was intended to study the evolution of materials used in seals and gaskets with exposure to biodiesel and biodiesel blends.

The following section details the results achieved within the first two tasks.

3.0 RESULTS

3.1 Task 1: Literature Survey of Biodiesel/Materials Integrity Precedence

The focus of the literature survey was to generate a compilation of previous biodiesel and materials-related research out of which a gap analysis could be conducted to reinforce the aims of the technical tasks. It was discovered in the literature search that materials other than pipe steel and specific elastomeric materials had not been studied with respect to biodiesel exposure. Moreover, the influence of feedstock had not been addressed but it was discovered that feedstock does have an effect on the final properties of the fuel even if each biodiesel follows ASTM standard specifications. The main variable worth addressing was the amount of saturation of the fatty acid chains which is variable from feedstock to feedstock. This later became an extended dimension of matrix after a meeting with members of The National Biodiesel Board.

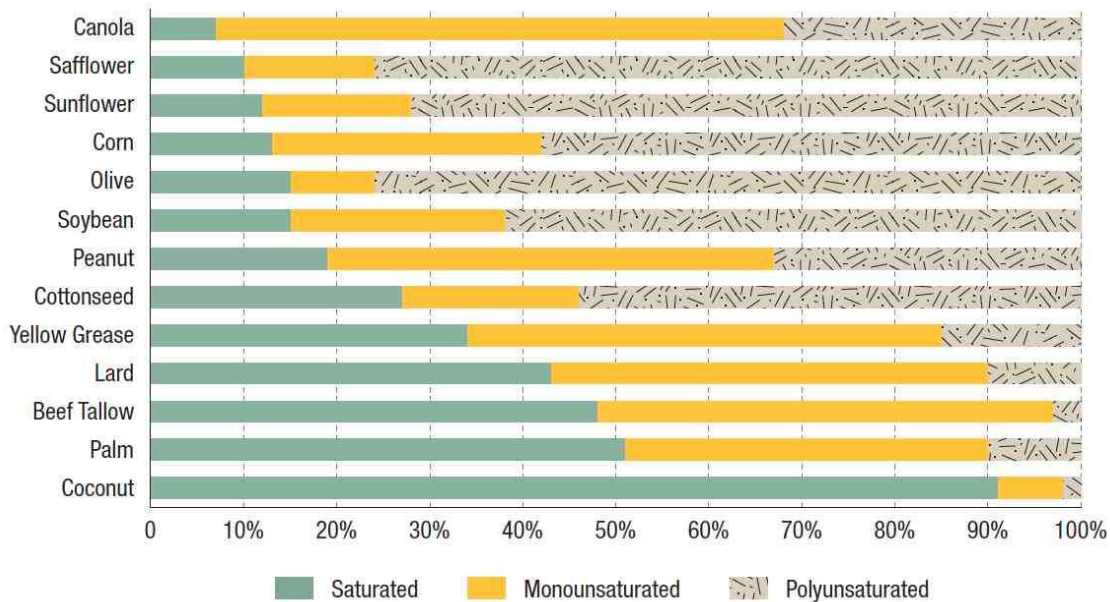


Figure 2. Plot of fat saturation content with respect to different feedstocks [4].

Also under the guise of Task 1, preliminary evaluation of electrochemical testing techniques was conducted. It was assumed there would be some difficulty in measurement of electrochemical signals (indicative of corrosion) in a highly resistive fluid such as biodiesel.

It was demonstrated that the employment of small size electrode made it possible to perform electrochemical measurements in simulated grade fuel ethanol (SFGE) [6]. However, the initial attempt in using the same technique did not generate meaningful results for carbon steel in biodiesel. The following figures are examples of data collected during these trials. The first is a cyclic potentiodynamic curve that exhibits discernible characteristics of an adequate polarization; however, the coupled figure which depicts the same plot on a linear scale shows that the sample in solution behaved only as a resistor. This behavior suggests that the solution resistance was too high to make any meaningful polarization measurements.

Cyclic Potentiodynamic Polarization

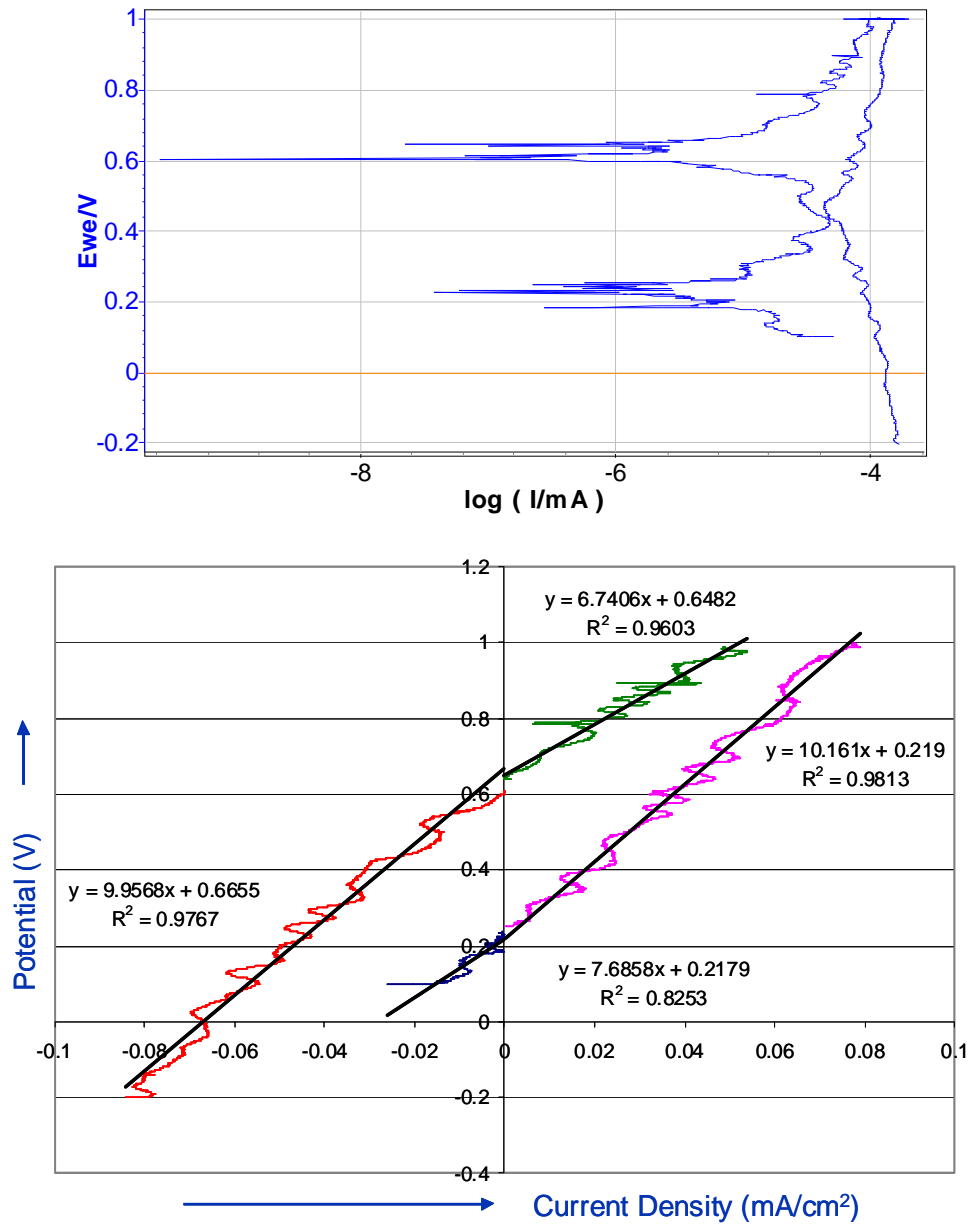


Figure 3. (top) Typical potential versus logarithm current plot of a cyclic potentiodynamic polarization curve. (bottom) The same data plotted on a linear scale showing that the polarization in the top plot was little more than a documentation of the solution resistance.

Since initial attempts at electrochemical techniques provided no usable results, efforts were taken to measure the conductivity of biodiesel and its blends to discern if any electrochemical measurement may be possible. The results were compared to pre-existing work with synthetic fuel grade ethanol (SFGE).

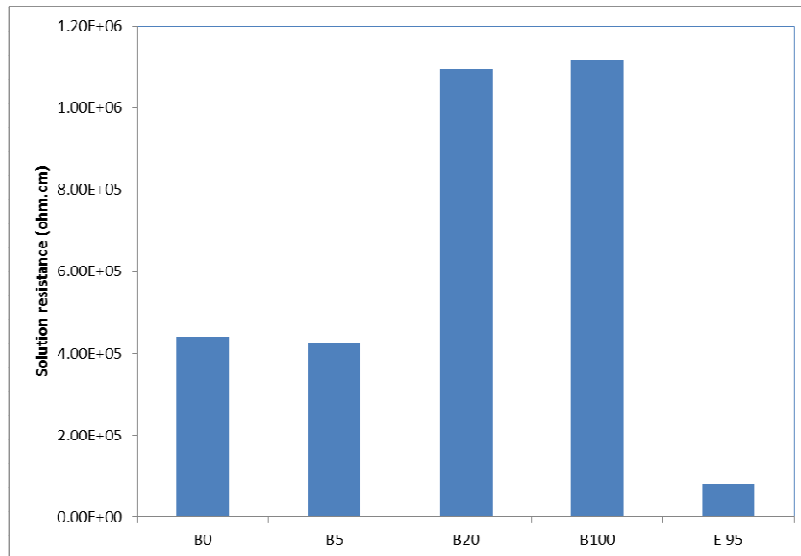


Figure 4. Comparison of the solution resistance obtained in EIS for petrodiesel (B0), biodiesel blends and E95.

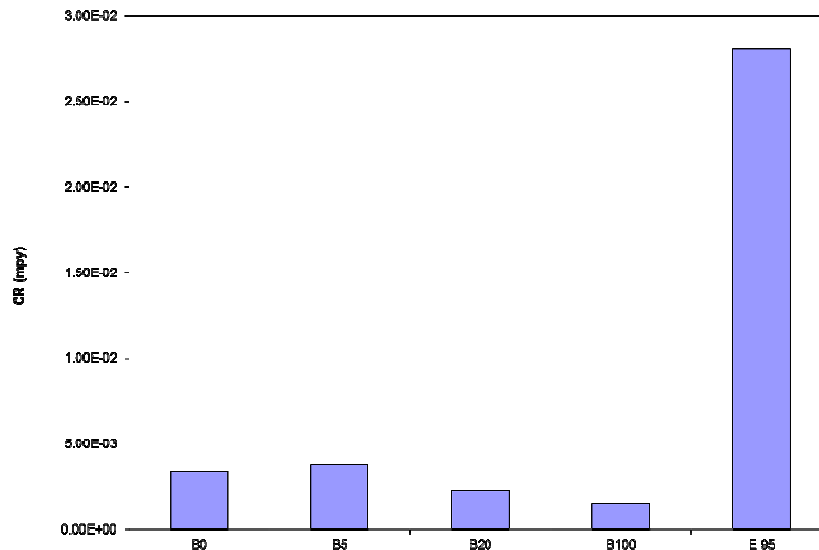


Figure 5. Comparison of the corrosion rates converted from polarization resistance obtained in EIS for petrodiesel (B0), biodiesel blends and E95.

Efforts were also made to explore the possibility of using techniques such as two-electrode electrochemical impedance spectroscopy (EIS) and multi-electrode arrays with supporting electrolytes that are used frequently in less conductive aqueous environments to measure corrosion rate. Results of this effort have been included in a report from Dr. Feng Gui on the contaminant effect on biodiesel properties (“Setting Safe Limits on Biodiesel Constituents for Pipeline Integrity”).

3.2 Task 2: Corrosion Inhibition Evaluation

Two types of biodiesel were supplied by a pipeline operator: one based on fresh vegetable oil and the other based on used vegetable oil. The biodiesel from fresh vegetable oil was used in this work. Petrodiesel was also provided by an independent vendor and was used in a non-additive state.

For this testing a string of test cells were assembled and temperature controlled to 38 ± 1 °C per NACE TM-0172. Consistency of temperature was checked from the first cell to the last in the chain to make sure the temperature window was maintained. Examples of the test cell setup are pictured below.

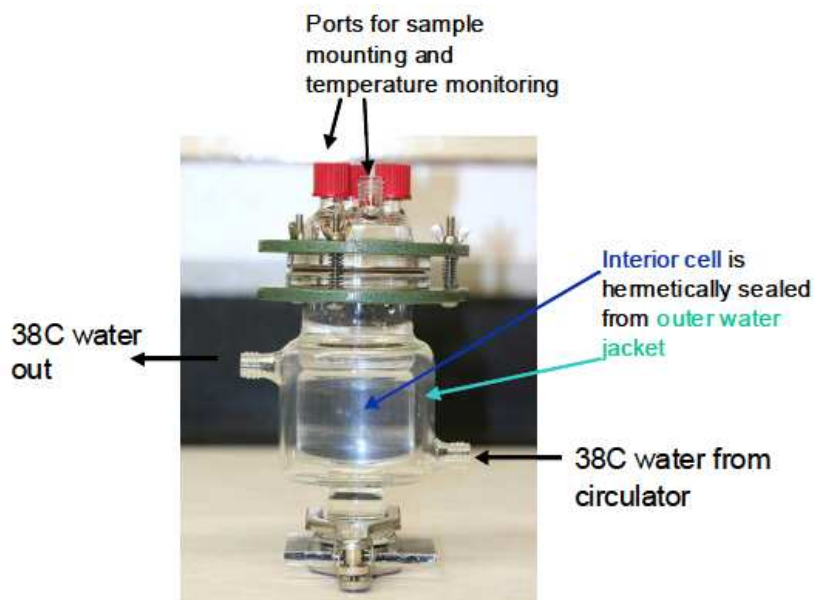


Figure 6. Typical jacketed test cell



Figure 7. Test cells for inhibitor testing in biodiesel.

Temperature was maintained using a circulating water bath and common automobile anti-freeze was used as the exterior coolant. The cells are jacketed glass cells which keep the inner chamber hermetically sealed from the jacket through which the coolant is passed. CS1018 test specimens were suspended from the top of the cell and completely submerged in the biodiesel (or petrodiesel). Batches of samples were exposed to the fuel environment for 30 days. After the duration of the exposure, specimens were cleaned and weighed for any change in weight brought on by the immersion in the fuel source. Each sample was also visually inspected per NACE TM-0172 for surface pitting. Test conditions were run in duplicate. Each inhibitor was evaluated in biodiesel as well as petrodiesel with controls of each fuel type as well. The following table summarizes the test conditions and the averaged results for each set of exposure tests.



Table 1. Tabulated results for common petrodiesel corrosion inhibitors in both biodiesel and petrodiesel fuels.

Test Set	Fuel type	Type of Inhibitor	Quantity of Inhibitor	Weight Change (grams)	Corrosion Rate (mm/yr)	# of pits
1	B100	No Inhibitor	0	0.0000	0.0000	0
1a	B0	No Inhibitor	0	0.0002	0.0009	0
2	B100	T3232	5 ppm	0.0001	0.0004	0
2a	B0	T3232	5 ppm	0.0001	0.0004	0
3	B100	T3232	10 ppm	0.0000	0.0000	0
3a	B0	T3232	10 ppm	0.0000	0.0000	0
4	B100	EC5407A	5 ppm	0.0001	0.0004	0
4a	B0	EC5407A	5 ppm	0.0001	0.0004	0
5	B100	EC5407A	10 ppm	0.0000	0.0000	0
5a	B0	EC5407A	10 ppm	0.0001	0.0004	0
6	B100	DCI-30-n	5 ppm	0.0000	0.0000	0
6a	B0	DCI-30-n	5 ppm	0.0000	0.0000	0
7	B100	DCI-30-n	10 ppm	0.0000	0.0000	0
7a	B0	DCI-30-n	10 ppm	0.0000	0.0000	0

As can be seen from the summarized results, the effect of corrosion inhibitors is not clearly identified due solely to the fact that uninhibited fuel exhibited corrosion rates near zero as well. One take away is that common petrodiesel corrosion inhibitor compounds may be used in biodiesel without fear of any adverse reactions with the fuel composition with respect to increases in corrosivity of the fuel itself. As elucidated by work completed by Dr. Gui, the interface between the fuel and the separated water phase is the area of higher corrosion concern. The work performed under this contract reinforces pre-existing notions that bulk fuel is not of great concern as a corrosion threat.



4.0 GENERAL DISCUSSION

The overarching conclusion from the work that was completed under this contract is that the corrosivity of bulk biodiesel is not of immediate concern from a pipeline materials integrity standpoint. One caveat to this conclusion is that auxiliary materials systems were not addressed and thus cannot be commented upon in this context. The corrosion rates generated in Task 2 that reflect the efficacy of common petrodiesel inhibitors were very near zero both with and without corrosion inhibition. This makes some intuitive sense since as we discovered that bulk biodiesel is a highly resistive medium.

5.0 SUMMARY/ FUTURE WORK

A gap analysis was conducted under the guise of a literature survey to begin the progress of this research. From the results of this task, the matrix was augmented to account for feedstock variability. This literature search also highlighted the relevance of our other proposed materials related testing tasks. Notably the concern for understanding the roles that certain materials (Cu-containing alloys, e.g.) play on the degradation of the fuel itself.

From this, it seems prudent that the remaining tasks that were not addressed due to the cancellation of this program are still relevant technical problems. The proposed tasks 3 and 4, which cover the interaction between Cu-alloys and biodiesel fuel blends and the evolution of elastomer properties, respectively, may still provide valuable insight into possible integrity threats in the scale up of the transportation of biodiesel through pipeline systems.

Further biodiesel and material compatibility evaluation suggested:

- Discern the effects of Cu-alloy degradation of the fuel
- Simultaneous documentation of the effect of biodiesel exposure to Cu-alloy samples
- Investigation of the evolution of elastomeric materials with prolonged exposure to biodiesel.



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